The crystal structure and bonding of lorandite, $Tl_2As_2S_4$*

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Auszug

Die Kristallstruktur von Lorandit $Tl_2As_2S_4$, in der AsS_3-Tetraeder zu spiralförmigen Ketten parallel [010] angeordnet und die Ketten durch Tl-Atome verbunden sind, wird bestätigt und bis zu $R = 0,09$ verfeinert. Die Gitterkonstanten sind $a = 12,28$ Å, $b = 11,30$ Å, $c = 6,10$ Å, $\beta = 104°5'$; $Z = 4$. Raumgruppe ist $P2_1/a$. Die S-Atome werden von den As- und Tl-Atomen in den Ecken schwach deformierter Tetraeder umgeben. S-Atome, die aufeinanderfolgende As-Atome in der Kette verbinden, haben außerdem noch zwei Tl-Atome zu Nachbarn. Jedes S-Atom, das nur an ein As-Atom gebunden ist, hat drei nächste Tl-Nachbarn; sein Abstand zum As-Atom ist auffallend klein (2,08 und 2,20 Å entsprechend den zwei nicht-äquivalenten As-Atomen der Struktur).

Jedes Tl-Atom liegt einer der AsS_3-Pyramidenketten näher als den übrigen; die S-Umgebung der Tl-Atome bildet deformierte tetragonale Pyramiden mit Tl in der Spitze.

Lage und Ausbildung der Spaltbarkeit hängt unmittelbar von Zahl und Typ der Bindungen zwischen den Ketten ab. Die kurzen (As—S)-Abstände weisen darauf hin, daß diese Bindungen bis zu einem gewissen Grad den Charakter von π-Bindungen haben. Die geringe Differenz der Elektronegativitäten von Tl und S, die scheinbare Wechselwirkung zwischen benachbarten Tl-Atomen und der Vergleich mit Tl-haltigen organischen Verbindungen legen die Annahme nahe, daß zwischen den Tl-Atomen und den AsS_3-Ketten kovalente Kräfte bestehen.

Abstract

Lorandite ($Tl_2As_2S_4$) is monoclinic with $a = 12.28(1)$ Å, $b = 11.30(1)$ Å, $c = 6.101(6)$ Å, $\beta = 104°5'(2')$, space group $P2_1/a$, $Z = 4$. The crystal structure, consisting of spiral chains of AsS_3 pyramids oriented parallel to [010] and connected by Tl atoms, has been confirmed and refined by full-matrix least-squares analysis of three-dimensional diffractometer data to give a value of the conventional residual index of 0.09. The positions of the S and As atoms are mark-

* Dedicated to Professor M. J. Buerger on the occasion of his 70th birthday.

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edly different from those reported in the literature. The present study has shown that the bonds from the two non-equivalent As atoms to the non-bridge S are quite short (2.08 Å and 2.20 Å), that each S is tetrahedrally coordinated to As and Tl and that each Tl position is more closely related to one AsS_3 pyramid chain than to adjacent chains, the nearest-neighbor S environment of each being a distorted square-pyramidal configuration.

The development of cleavage in lorandite is directly related to the number and type of the interchain bonds. It is suggested that the short As non-bridge S distances in this mineral and in other sulfosalts indicate some degree of π-bonding character in these bonds. Finally, the small difference in the electronegativities of Tl and S, the apparent bonding interaction between adjacent Tl atoms and comparisons with Tl-bearing organic compounds suggest the that Tl atoms are bound by covalent forces to the AsS_3-pyramid chains.

Introduction

The sulfosalt lorandite, $Tl_2As_2S_4$, is found in low-temperature mineral assemblages in association with orpiment, realgar, pyrite and certain other sulfide minerals; the most familiar locality being Allchar, Macedonia. It has monoclinic symmetry with $a = 12.27$ Å, $b = 11.34$ Å, $c = 6.11$ Å, $\beta = 104°12'$ (HOFMANN, 1933), space group $P2_1/a$, $Z = 4$. The mineral is deep red and, because of the prominent development of cleavage [(100) excellent, ($\bar{2}$01) very good, (001) good], it appears flexible in hand specimen, separating easily into cleavage lamellae and fibres (DANA's *System of mineralogy*, 1946).

Table 1. *Positional parameters of* ZEMANN *and* ZEMANN

	x	y	z
Tl(1) in 4e	0.051	0.313	0.160
Tl(2) in 4e	0.101	0.056	0.732
As(1) in 4e	0.190	0.820	0.237
As(2) in 4e	0.151	0.585	0.554
S(1) in 4e	0.125	0.320	0.750
S(2) in 4e	0.150	0.580	0.200
S(3) in 4e	0.125	0.790	0.510
S(4) in 4e	0.200	0.030	0.200

The crystal structure of lorandite was determined from $h0l$ and $hk0$ reflections (ZEMANN and ZEMANN, 1959), giving the positional parameters in Table 1, and consists essentially of spiral chains of AsS_3 pyramids oriented parallel to [010] and linked together by irregularly coordinated Tl atoms. KNOWLES (1965) reported on a refinement of

the structure based on three-dimensional intensity data, suggesting that the S and As positions were poorly defined in the original study and that the Tl atoms appeared to be in twofold coordination with S.

Experimental

The present study was made on material from Allchar obtained through David New Minerals, Hamilton, Montana. Some difficulty was encountered in obtaining a single crystal from the hand specimen because the mineral deforms very readily when handled so that crystals reduced to a suitable size invariably have bent or twisted cleavage surfaces. The crystal selected was a tabular (010) cleavage fragment bounded by plane surfaces, 0.003 cm thick with a calculated volume of $0.11 \cdot 10^{-6}$ cm³; it was mounted on the b axis to minimize possible errors in the absorption correction. Reflections recorded on precession camera films of the crystal did not show any evidence of deformation. The systematic absences on these films confirmed the accepted space group for lorandite, $P2_1/a$. The lattice parameters, obtained by least-squares refinement of twelve centred reflections of the crystal on a four-circle diffractometer, are $a = 12.276(12)$ Å, $b = 11.299(2)$ Å, $c = 6.101(6)$ Å, $\beta = 104°5'(2')$—the standard deviations are in parentheses—and compare quite favourably with published data.

The x-ray intensity data for the structure analysis were taken on a Picker facs 1 four-circle diffractometer system at the University of Western Ontario. All hkl and $h\bar{k}l$ reflections with $2\theta \geq 45°$ were measured using a scintillation detector, Zr-filtered $MoK\alpha$ ($\lambda = 0.7107$ Å) radiation and the 2θ-scan technique: 40 second stationary background counts, peak-base widths of $2.0°$ 2θ (uncorrected for dispersion) and a scanning rate of $0.5°$ per minute. The resulting data were processed by a data-correction routine which corrected for background, Lorentz and polarization effects, and absorption, and assigned standard deviations (σ) to the corrected data based on the summed variances of the counting rates of the peaks and associated backgrounds. Transmission factors for the absorption correction were calculated by the analytical method of DE MEULENAER and TOMPA (1965) using a value for the linear absorption coefficient of 485.6 cm⁻¹. The calculated transmission factors varied from 0.10 for $31\bar{6}$ to 0.22 for 12 2 1. Each reflection whose intensity was less than the associated background plus 3σ was given zero intensity. The final data list contained 1078 reflections of which 404 were "unobserved".

Crystal-structure investigation

At this stage in the investigation the author was unaware that the structure had been confirmed by Knowles (1965), and it was considered desirable to redetermine the structure independently of the earlier work.

The structure factors were converted to normalized structure factors, E, using program FAME (R. B. K. Dewar, Illinois Institute of Technology, Chicago), and, since the structure must be centrosymmetric, the phases of those normalized structure factors with $E \geqslant 1.5$ were assigned by a reiterative application of Sayre's equation using program REL 1 (adapted from R. E. Long, Ph. D. Thesis, University of California, Los Angeles, 1965). E maps, prepared from the solution with the largest consistency index (0.998), clearly indicated two Tl positions, two probable and one possible As positions and various possible S positions. A value of the conventional residual index, R, of 0.33 was obtained using a trial set from these positions. A F_o Fourier synthesis resolved all the positional ambiguities, giving a set of atomic positions which resulted in a lowering of the residual index to 0.23 and which proved to be equivalent to the accepted structure of lorandite; the As and S atoms being associated to form spiral chains of AsS_3 pyramids oriented parallel to [010] (Figs. 1a and 1b) with two nonequivalent Tl atoms seemingly irregularly coordinated between them.

The structure was refined further by full-matrix, least-squares refinement using program RFINE (L. Finger, Geophysical Laboratory, Washington). RFINE minimizes the function $\Sigma w (|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$, F_o is the observed and F_c the calculated structure factor, and calculates a conventional residual index, $\Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and a weighted residual index, $[\Sigma w (|F_o) - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. The scattering curves for Tl and As were taken from Cromer and Mann (1968) and that for S^{2-} computed for a nine parameter fit from data in the *International tables for x-ray crystallography*, Vol. III; the anomalous dispersion coefficients of Cromer (1965) for Tl, As and S were included. Isotropic and anisotropic thermal parameters were added successively to the refinement. However, the values of the anisotropic thermal parameters for the S atoms were somewhat erratic and inconsistent, suggesting that they were reflecting limitations in the data set rather than true thermal motions of the atoms, and the refinement was limited to anisotropic thermal parameters for Tl and As atoms and isotropic thermal parameters for S atoms. The values of the conven-

tional and weighted residual indices obtained for the non-zero intensities used are all isotropic, 0.105 and 0.114, and anisotropic Tl and As and isotropic S, 0.094 and 0.098. According to the procedure for

a)

b)
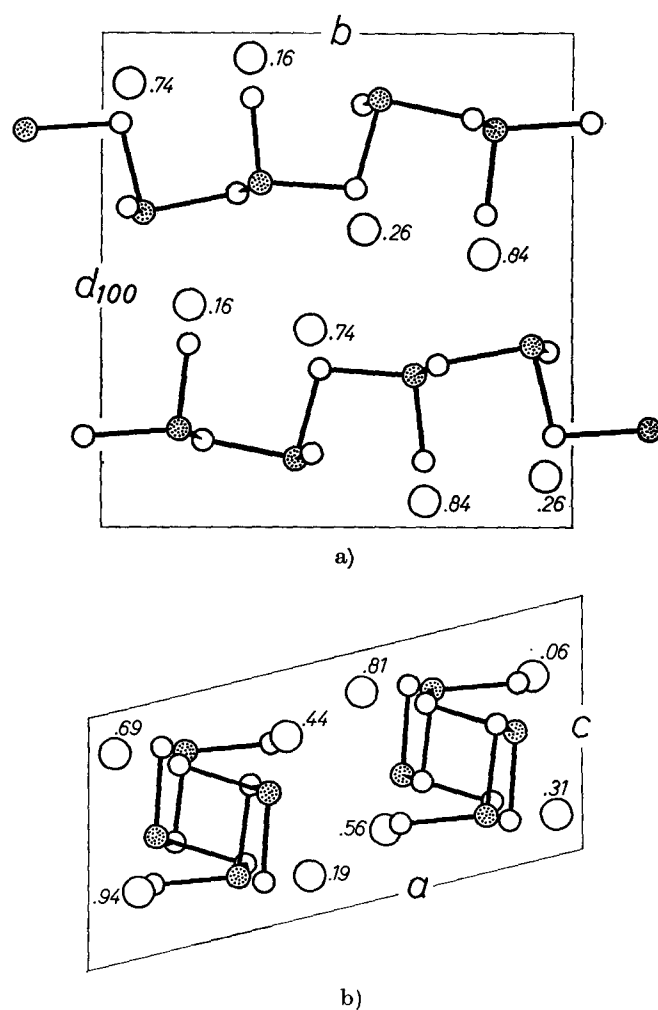
Fig. 1. The crystal structure of lorandite projected parallel to a) c axis, b) b axis; Tl: large open circles with the height in the projection indicated, As: small stippled circles, S: small open circles

testing weighted residuals (HAMILTON, 1965), the value of the residual index for the latter refinement is significant, compared to that using isotropic thermal parameters only, at the 0.005 level. The positional

Table 2. *Positional and thermal parameters* (standard deviations in parentheses)

Position	x	y	z	B_{11} (B)	B_{22}	B_{33}	B_{13}
Tl(1)	0.0519(3)	0.3121(4)	0.1619(6)	2.6(2)	2.1(2)	1.3(2)	3.4(6)
Tl(2)	0.1009(3)	0.0560(4)	0.7357(7)	3.0(2)	2.1(2)	1.3(2)	4.1(6)
As(1)	0.1960(8)	0.8353(9)	0.2266(15)	2.7(5)	1.5(5)	0.7(4)	1.8(1.5)
As(2)	0.1361(8)	0.5865(8)	0.5320(16)	3.3(5)	1.3(5)	1.3(5)	7.2(1.6)
S(1)	0.131(2)	0.316(3)	0.721(5)	3.3(6)			
S(2)	0.147(2)	0.553(2)	0.183(4)	1.6(4)			
S(3)	0.174(2)	0.786(2)	0.577(4)	2.2(5)			
S(4)	0.183(2)	0.038(2)	0.272(4)	1.7(5)			

and thermal parameters, and associated standard deviations for this refinement are given in Table 2.

The refinement was terminated when the changes to the positional and anisotropic thermal parameters were in the sixth places and the ratios of the changes in these parameters to the errors in the parameters were less than 0.005. The observed and calculated structure factors are given in Table 3. The refined structure was checked with F_o and F_o—F_c Fourier maps; no significant residual peaks were detected.

Discussion of the structure

The positional parameters determined in the present study show marked discrepancies from those reported in the original work (ZEMANN and ZEMANN, 1959). As expected, the discrepancies are least for the heavy Tl atoms and greatest for the lighter S atoms. Thus, although the structure was outlined correctly, the bond distances and bond angles reported for the spiral chains of AsS_3 pyramids have little relation to the actual values. The ranges of the interatomic distances quoted by KNOWLES (1965) are similar to those of the present study, suggesting that the positional parameters of the two refinements would be quite comparable.

Some interatomic distances and bond angles of interest are given in Tables 4 and 5 respectively (the atom identification labels are consistent with the usage in Fig. 2; atoms marked by an asterisk are located in adjacent unit cells). The As—S bonds which form bridge bonds between the AsS_3 pyramids are similar in length (2.29 Å to 2.32 Å) to the average bridge bond (2.31 Å) obtained from a survey of well refined sulfosalt structures (TAKÉUCHI and SADANAGA, 1969). However, the non-bridge As—S bonds are somewhat shorter (2.08 Å

Table 3. *Observed and calculated structure factors*

Column 1

h k l	Fo	Fc
0 0 2	523	473
3	316	287
4	232	210
0 1 2	174	149
3	278	243
4	200	177
5	201	188
0 2 1	130	125
2	82	72
3	182	165
4	226	219
5	120	129
6	119	127
0 3 1	291	309
2	105	97
3	193	178
0 4 1	24	25
2	32	47
3	69	60
6	33	18
0 5 1	175	181
2	71	72
3	114	110
0 6 1	169	176
2	116	128
3	99	93
4	108	106
5	74	103
0 7 1	31	57
2	138	147
3	134	131
4	31	62
5	196	204
0 8 0	386	442
1	30	52
2	258	254
3	127	141
4	76	77
0 9 1	84	104
2	91	99
3	40	71
4	147	142
0 10 2	150	161
3	98	107
0 11 1	145	177
1 1 0	53	48
1	70	69
2	164	158
3	110	99
4	195	184
6	152	157
-1	154	121
-2	300	263
-3	288	265
-4	152	133
-5	77	39
-6	174	158
1 2 1	355	385
2	60	62
3	117	113
4	163	168
5	72	98
-1	218	191
-2	199	175
-5	78	80
-6	102	80
1 3 0	320	330
1	208	214
2	208	200
3	276	271
4	53	6
5	74	89
6	77	98
-2	189	163
-3	54	29
-5	132	131
1 4 0	466	500
5	219	235
-1	66	67
-2	537	516
-3	249	226
-4	351	336
-5	250	260
-6	121	125
1 5 0	156	165
1	161	174
2	168	172
3	213	223
5	64	69
-1	141	148
-2	163	154
-4	187	180
1 6 0	62	69
1	179	202
2	231	223
3	139	142
4	129	130

Column 2

h k l	Fo	Fc
1 6 -1	220	216
-4	81	80
-5	73	54
1 7 1	120	128
2	57	51
-1	180	181
-2	109	113
-4	95	94
-5	77	74
1 8 3	95	106
1 9 0	60	70
2	70	78
4	146	142
-2	101	108
-3	100	96
-4	90	107
1 10 1	151	185
1 11 0	174	202
2	108	114
1 12 0	73	77
2 0 0	88	111
1	144	190
2	312	359
3	179	186
5	234	221
-1	49	87
-2	250	240
-4	288	256
-5	323	293
-6	276	262
2 1 0	122	130
1	311	338
4	168	157
5	133	122
6	79	66
-1	70	62
-2	475	426
-4	111	97
-5	75	79
2 2 0	83	72
1	120	125
2	78	71
-1	355	323
-2	84	69
-3	283	257
-4	162	149
2 3 0	51	47
1	113	122
2	247	258
3	237	227
4	111	116
-1	156	148
-2	202	182
-3	152	133
-4	121	107
-6	199	209
2 4 0	48	31
1	49	50
3	76	64
2 5 0	133	135
1	180	199
2	272	263
3	202	205
4	202	207
5	77	95
-1	201	197
-2	212	204
-4	152	152
2 6 1	153	165
-1	263	251
-2	76	85
-3	145	148
-4	203	208
-5	80	88
2 7 0	226	244
1	75	91
-1	144	139
-2	245	233
-4	194	186
2 8 0	103	133
1	99	104
2	214	205
3	185	173
4	66	63
-2	98	76
-4	160	163
2 9 1	186	196
-2	215	195
2 10 0	57	67
2	81	73
-1	117	146
-3	155	162
3 1 0	106	107
1	232	254
2	210	239

Column 3

h k l	Fo	Fc
3 1 3	212	232
4	59	26
-1	421	428
-2	125	138
-3	205	199
-4	70	56
-5	68	83
3 2 0	93	98
1	85	93
1	126	136
2	136	143
4	166	189
5	66	76
-1	126	114
-3	166	150
-4	220	213
-5	209	221
-6	138	146
3 3 0	153	156
2	213	226
3	224	227
4	81	82
5	211	223
-1	145	141
-2	185	154
-3	100	95
-4	256	238
-6	112	111
3 4 0	412	431
1	122	143
2	197	193
-1	70	71
-2	260	240
-3	236	204
-4	133	129
-6	119	140
3 5 0	222	221
1	124	130
2	121	121
3	187	186
4	123	105
5	98	111
-1	98	93
-2	173	158
-3	129	116
-4	179	159
3 6 1	133	156
2	130	131
3	80	78
4	190	200
-3	161	167
-5	92	116
3 7 1	115	118
2	68	73
3	139	121
-1	179	183
-3	85	71
3 8 1	65	70
2	76	78
3	66	21
-1	120	118
3 9 0	84	95
1	163	178
2	114	109
3	91	98
-1	210	221
-2	77	68
-3	132	151
3 10 2	90	65
-1	74	79
3 11 1	102	103
-1	75	72
-2	61	54
4 0 0	246	318
1	167	203
3	233	267
5	254	268
-1	56	94
-2	223	276
-3	229	265
-4	440	421
-5	165	149
-6	94	68
4 1 0	386	405
1	188	202
2	102	105
3	240	268
-2	227	242
-3	119	140
-4	75	55
-5	132	129
4 2 0	233	244
1	223	252
2	199	201
4	118	130
-1	287	270
-3	124	122

Column 4

h k l	Fo	Fc
4 2 -4	68	49
-6	92	98
4 3 1	85	88
3	83	84
4	130	149
-1	190	191
-2	69	57
-3	262	248
-4	65	49
-5	94	110
-6	70	92
4 4 2	51	57
-2	86	93
4 5 1	80	85
3	62	64
4	62	64
-1	234	230
-3	278	260
4 6 0	186	190
1	120	124
2	116	109
3	80	81
4	84	75
-2	88	71
-3	80	87
-5	118	128
4 7 0	209	229
1	230	233
2	150	133
3	199	176
-1	64	49
-2	164	170
-3	92	94
4 8 0	132	132
3	159	132
-2	227	218
-3	80	79
-4	223	238
4 9 0	149	154
1	61	66
3	140	125
-1	109	90
-3	86	70
4 10 0	67	80
1	123	139
2	176	165
-1	233	241
-2	81	68
-3	78	61
5 1 0	72	80
1	56	66
2	126	144
4	88	96
-1	98	99
-2	123	138
-3	92	121
-6	162	163
5 2 0	224	221
1	42	42
2	120	118
-1	123	120
-2	65	69
-3	236	256
5 3 0	215	209
1	175	182
-1	224	213
-2	394	366
-4	262	260
-5	132	149
-6	92	69
5 4 0	46	47
1	421	419
2	116	96
3	297	300
4	67	75
-1	120	113
-3	162	139
-4	224	208
-5	135	139
-6	161	180
5 5 0	88	88
1	146	161
2	58	69
3	56	34
-1	145	144
-2	321	298
-3	92	77
-4	92	90
5 6 0	131	129
1	67	72
2	60	51
-1	294	280
-2	133	132
-3	264	263

Column 5

h k l	Fo	Fc
5 6 -5	122	155
5 7 0	98	106
2	189	175
4	123	107
-1	61	65
-2	138	140
-4	76	70
5 8 3	76	50
5 9 0	56	67
2	61	49
5 10 0	94	102
-3	99	100
5 11 0	99	93
-1	115	120
6 0 0	80	82
1	364	435
3	90	111
4	62	62
-1	270	336
-2	222	285
-3	155	178
-4	143	168
-5	114	122
-6	118	85
6 1 0	82	86
2	50	45
3	122	132
4	62	71
-1	87	96
-2	184	191
-3	177	208
-4	189	209
-5	67	77
-6	230	230
6 2 0	63	56
1	97	107
2	193	201
4	131	156
-2	101	97
-3	119	133
-5	171	206
-6	86	64
6 3 0	70	62
2	124	122
3	106	106
-1	266	257
-2	190	192
-3	107	103
-5	96	115
-6	103	117
6 4 4	69	60
6 5 0	54	40
1	136	145
3	124	116
-1	245	228
-2	99	93
-3	123	121
6 6 -1	109	102
2	205	190
3	99	85
4	115	121
-1	130	112
-5	109	135
6 7 1	105	97
2	67	55
3	141	127
-1	99	97
-2	75	74
6 8 0	97	96
1	229	209
-1	205	186
-2	182	178
-3	90	77
-4	103	102
6 9 0	127	120
-2	93	60
6 10 -1	57	56
-2	59	52
7 1 0	81	80
2	71	84
3	145	162
4	144	141
-1	233	238
-2	179	197
-5	172	211
7 2 0	261	254
1	117	131
2	203	208
4	71	77
-1	201	191
-3	187	217
7 3 0	77	79
1	205	207
2	51	27

Column 6

h k l	Fo	Fc
7 3 3	95	87
4	77	77
-1	140	121
-2	74	82
-5	60	53
-6	140	176
7 4 3	148	142
-1	204	189
-2	109	110
-3	143	127
-4	302	300
-5	111	101
7 5 0	151	123
1	81	95
2	89	83
3	90	77
-1	126	116
-3	162	153
-5	82	80
7 6 0	171	174
1	105	91
2	158	133
-1	143	135
-2	59	48
-3	76	78
7 7 3	62	63
-1	90	83
-2	79	73
-3	94	104
7 8 2	64	54
-1	85	87
-2	80	72
7 9 1	124	106
-1	126	119
-3	134	130
7 10 0	93	106
-1	105	102
8 0 0	79	107
3	189	191
-1	70	88
-2	164	197
-4	128	144
-5	117	137
-6	108	120
8 1 2	79	93
3	71	70
-1	198	198
-2	65	63
-3	61	58
-4	94	127
8 2 0	187	180
1	69	72
-1	146	131
-2	117	119
-3	255	286
-5	171	183
8 3 0	202	187
2	134	115
3	112	95
-2	112	108
-3	61	63
8 4 2	55	45
-1	90	90
-2	64	54
-3	54	25
8 5 0	211	203
1	59	70
2	145	144
-1	93	79
-2	128	127
-3	76	77
-4	77	84
-5	85	109
8 6 0	186	176
3	58	21
-2	88	85
-3	259	247
-4	93	102
8 7 0	94	89
-1	157	135
-2	109	101
-3	89	79
-4	103	117
8 8 1	209	182
-1	84	80
8 9 -1	120	112
9 0 0	153	144
-1	62	55
-3	202	213
-4	68	77
-5	82	88
9 2 0	56	21
2	131	125

Column 7

h k l	Fo	Fc
9 2 -3	131	159
-4	70	106
-5	158	191
9 3 1	139	130
2	52	18
3	138	127
-2	49	54
-3	93	78
-4	80	80
9 4 0	50	29
1	243	212
-1	251	228
-2	267	237
-3	226	204
-4	125	137
9 5 0	72	73
1	122	108
-2	52	42
-3	132	128
9 6 0	87	74
2	146	133
-3	101	101
9 7 0	112	86
1	56	17
-1	129	99
-2	167	143
-3	66	59
9 8 -1	95	90
-3	77	52
10 0 2	108	85
-1	107	116
-2	76	93
10 3 0	66	57
-1	120	100
-2	120	124
-3	63	54
-5	155	181
10 4 -3	53	36
10 5 0	52	30
2	68	83
-2	86	71
-3	55	50
10 6 -1	89	75
10 7 -1	144	112
-2	89	99
-3	80	78
11 1 0	215	196
2	114	115
-2	69	66
-3	50	17
11 2 -2	56	63
-3	116	118
-4	63	91
11 3 0	92	72
1	54	58
-1	187	142
-3	166	165
-4	99	115
11 4 1	128	123
-1	107	95
-4	77	68
11 5 -1	165	128
11 6 0	84	68
-2	114	98
12 0 0	63	76
1	77	63
-1	130	145
-3	170	163
12 1 1	68	57
-2	100	93
-3	86	88
12 2 0	55	64
1	77	65
-2	56	56
-3	62	61
12 3 0	176	146
-2	131	128
12 5 -2	177	150
13 1 -2	104	110
13 2 -2	168	158

Table 4. *Interatomic distances in lorandite*
(standard deviations in parentheses)

As(1)—S(1)	2.08(1) Å	Tl(1)—S(1)	3.31(3) Å	Tl(2)—S(1)	2.97(3) Å
As(1)—S(3)	2.29(3)	Tl(1)—S(1)*	3.07(3)	Tl(2)—S(2)	3.014(5)
As(1)—S(4')*	2.32(3)	Tl(1)—S(2')	2.96(2)	Tl(2)—S(3')	3.93(3)
As(2)—S(2)	2.20(2)	Tl(1)—S(2''')	3.19(2)	Tl(2)—S(4)	3.19(2)
As(2)—S(3)	2.30(3)	Tl(1)—S(3)	3.36(1)	Tl(2)—S(4)*	3.23(2)
As(2)—S(4)	2.32(1)	Tl(1)—S(3''')	3.69(2)	Tl(2)—S(3''')	3.89(1)
		Tl(1)—S(4)	3.48(2)	Tl(2)—S(4'')	3.63(1)
S(1)—S(3)	3.35(2)	Tl(1)—Tl(2)*	4.032(6)	Tl(2)—Tl(2'')	3.541(6)
S(1)—S(4')*	3.38(3)				
S(2)—S(3)	3.52(3)				
S(2)—S(4)	3.47(2)				
S(3)—S(4')*	3.42(3)				
S(3)—S(4)	3.31(3)				

Table 5. *Bond angles in lorandite*
(standard deviations in parentheses)

S(1)—As(1)—S(3')	100.2(1.1)°	As(1)—S(1)—Tl(1)	101.1(1.0)°
S(1)—As(1)—S(4')*	100.5(1.2)°	As(1)—S(1)—Tl(1)*	113.2(1.2)
S(3)—As(1)—S(4')*	95.9(1.0)	As(1)—S(1)—Tl(2)	103.2(1.2)
S(2)—As(2)—S(3)	102.9(1.1)	Tl(1)—S(1)—Tl(1)*	145.6(0.9)
S(2)—As(2)—S(4)	100.5(0.9)	Tl(1)—S(1)—Tl(2)	90.6(0.8)
S(3)—As(2)—S(4)	91.5(0.9)	Tl(1)*—S(1)—Tl(2)	83.7(0.8)
		As(2)—S(2)—Tl(1')	109.9(0.9)
S(1)—Tl(1)—S(1)*	145.6(0.9)	As(2)—S(2)—Tl(1''')*	94.7(0.9)
S(1)—Tl(1)—S(2')*	85.9(0.7)	As(2)—S(2)—Tl(2)	98.1(0.8)
S(1)—Tl(1)—S(2''')	131.1(0.7)	Tl(1')—S(2)—Tl(1''')*	100.4(0.6)
S(1)—Tl(1)—S(3)	60.3(0.6)	Tl(1')—S(2)—Tl(2)	133.9(0.8)
S(1)*—Tl(1)—S(2')*	79.6(0.8)	Tl(1''')*—S(2)—Tl(2)	113.2(0.8)
S(1)*—Tl(1)—S(2''')	76.7(0.7)	As(1)—S(3)—As(2)	101.1(1.1)
S(1)*—Tl(1)—S(3)	85.6(0.7)	As(1)—S(3)—Tl(1)	95.2(0.8)
S(2')*—Tl(1)—S(2''')	79.7(0.6)	As(1)—S(3)—Tl(2')*	98.4(0.8)
S(2')*—Tl(1)—S(3)	73.9(0.6)	As(2)—S(3)—Tl(1)	107.1(0.9)
S(2''')—Tl(1)—S(3)	150.4(0.6)	As(2)—S(3)—Tl(2')*	148.6(1.0)
S(1)—Tl(2)—S(2)	83.3(0.7)	Tl(1)—S(3)—Tl(2')*	95.2(0.6)
S(1)—Tl(2)—S(3')	147.1(0.7)	As(1')—S(4)—As(2)	102.1(1.0)
S(1)—Tl(2)—S(4)	88.2(0.7)	As(1')—S(4)—Tl(2)	87.3(0.8)
S(1)—Tl(2)—S(4)*	94.8(0.7)	As(1')—S(4)—Tl(2)*	102.3(0.9)
S(2)—Tl(2)—S(3')	72.8(0.6)	As(2)—S(4)—Tl(2)	122.5(0.9)
S(2)—Tl(2)—S(4)	67.5(0.6)	As(2)—S(4)—Tl(2)*	89.9(0.8)
S(2)—Tl(2)—S(4)*	77.0(0.6)	Tl(2)—S(4)—Tl(2)*	143.8(0.8)
S(3')—Tl(2)—S(4)	62.2(0.6)		
S(3')—Tl(2)—S(4)*	101.3(0.6)		
S(4)—Tl(2)—S(4)	143.8(0.8)		

and 2.20 Å) than the average for bonds of this type (2.26 Å) for other sulfosalt structures. The bond angles within the chains are within the ranges for bridged AsS_3 pyramids in sulfosalts, although the S(3)—As(1)—S(4) and S(3)—As(2)—S(4) bond angles are significantly smaller (95.9° and 91.5°) than the remainder, which fall in the range 100° to 103°.

In the present representation of the structure, each S atom is in tetrahedral coordination (Fig.2); the bridge S atoms are coordinated to two As and two Tl whereas the non-bridge S atoms are coordinated
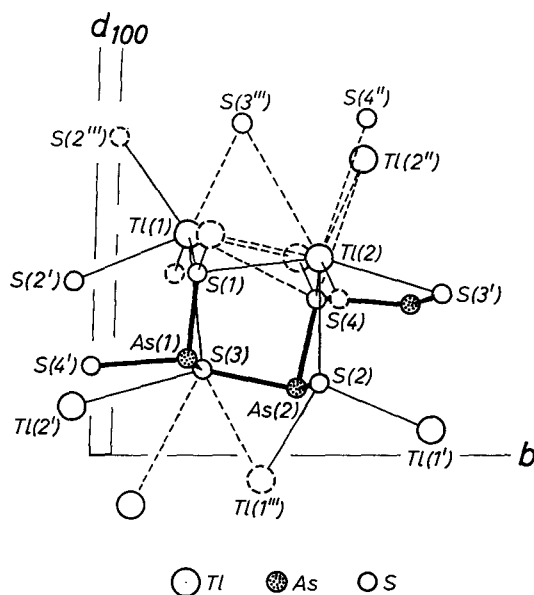
Fig.2. Tl and S environments in lorandite; the structure is projected parallel to c axis and rotated 5° about [100], dashed lines: interatomic distances greater than 3.40 Å, broken circles: atoms in unit cells above and below that represented

to one As and three Tl. Each tetrahedron is slightly distorted, but most of the bond angles do not depart too greatly from the ideal tetrahedral value.

Both Tl atoms are coordinated on the sides of the AsS_3 pyramid chains, adjacent to recesses formed in the chains. Each Tl position is more closely related to one chain than to neighboring chains. Although the S coordination polyhedra about the Tl atoms do appear irregular, closer inspection indicates many similarities in both positions. If an arbitrary limit of 3.40 Å is placed on the Tl—S distances,

each Tl atom is in fivefold coordination with S forming a flattened square pyramid. The bond distances and angles indicate considerable distortion from this ideal arrangement (Table 5). The Tl atoms are located beneath the base of each pyramid allowing for possible inter- actions with other Tl atoms and with more distant S and As atoms (Fig. 2). The closest Tl—S distances are, for both Tl(1) and Tl(2), to the non-bridge S atoms [S(1) and S(2)] and, these, presumably, correspond to the twofold coordination proposed by KNOWLES. How- ever, although these bond distances may represent the strongest bonding interactions, the Tl—S bond distances do show a gradational increase between 2.96 Å and 3.89 Å making definition of the nearest- neighbor coordination polyhedra quite arbitrary.

The environments of the Tl atoms in lorandite are somewhat similar to the probable environment of Tl in the isomorphic sulfosalts, hatchite (MARUMO and NOWACKI, 1967) and wallisite (TAKÉUCHI and OHMASA, 1968), in which the Tl,Pb(2) positions are coordinated to two S (with interatomic distances of 2.99 Å and 3.14 Å) and more distant S and As. In hatchite the Tl,Pb(2) positions approach each other as close as 3.78 Å. Short Tl—Tl distances have been reported also from the sulfides of thallium. Tl_2S has a distorted $Cd(OH)_2$ ($C6$ type) structure, in which each Tl is coordinated to three S, with Tl—S distances ranging from 2.61 Å to 3.15 Å, and to twelve Tl with Tl—Tl distances from 3.50 Å to 4.63 Å (KETELAAR and GORTER, 1939). In TlS, Tl apparently exists in both the Tl^+ and Tl^{3+} states (HAHN and KLINGLER, 1949). The Tl^{3+} is in tetrahedral coordination, with Tl—S distances of 2.60 Å, and the Tl^+ is in eightfold coord nation with Tl—S distances of 3.32 Å; Tl—Tl distances are 3.40 Å and 3.88 Å. In fact, in most of the investigated Tl-bearing sulfides and sulfosalts the Tl atoms have a tendency to interact with each other; in lorandite the closest Tl—Tl distances are 3.54 Å [Tl(2)—Tl(2)] and 4.03 Å [Tl(1)—Tl(2)].

The chains of AsS_3 pyramids are connected together in the lorandite structure by the Tl atoms. However the Tl atoms are associated more closely with one chain than with neighboring chains: of the ten Tl—S distances less than 3.40 Å in each formula unit, seven are within a single chain, only two connect directly chains lying within the same (100) plane and one connects chains lying within the same ($\bar{2}$01) plane: chains lying within the same (001) plane are connected directly by a strong Tl—Tl interaction. Clearly, the most cohesive bonding forces are within the chains (primarily As—S and Tl—S ones),

and the surfaces of weakness giving rise to cleavage in the crystals should pass between the chains. The development of cleavage in the mineral [(100) excellent, $(\bar{2}01)$ very good, (001) good] is just that predicted on the basis of the interchain bond distribution, since a (100) cleavage requires the disruption of only two Tl—S bonds and one Tl—Tl interaction per two formula units, a $(\bar{2}01)$ cleavage requires the disruption of four Tl—S bonds and one Tl—Tl interaction and a (001) cleavage requires the disruption of six Tl—S bonds (Fig. 3).
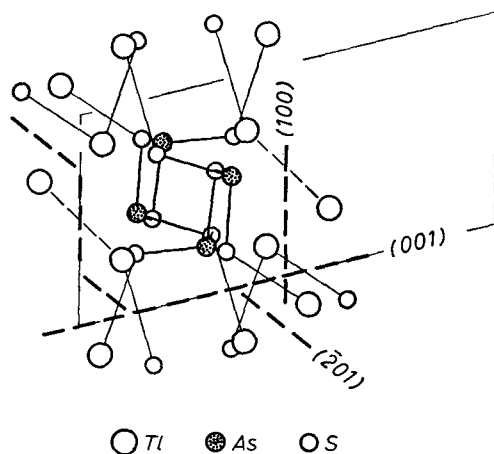
Fig. 3. The development of cleavage in lorandite

There are several interesting features in the structure of lorandite which are helpful to an understanding of the nature of the chemical bonding in the compound. These can be enumerated as follows:

(i)   the relatively short As—non-bridge S bonds

(ii)   the bond angles between the bridge S and As approach $90°$

(iii)   the apparent tetrahedral environment of S

(iv)   the apparent fivefold coordination of both Tl atoms by S

(v)   the close approach of the Tl atoms to each other.

The electron configuration of the valency electrons of the constituent atoms are Tl—$6s^2\ 6p^1$, As—$4s^2\ 4p^3$, S—$3s^2\ 3p^4$. It is generally accepted that the bonding within the groups of AsS_3 pyramids in sulfosalts is covalent; the principal evidence for this being the small difference in electronegativity of As(2.0) and S(2.5) and the similarity

of the As—S distances with the accepted covalent-bond 'ength. Assuming that the Tl atoms exist in the common 1 + oxidation state, each would donate the single $6p$ electron to form an effective $As_2S_4^{--}$ ligand group, so that there are 36 electrons available for the 16 single bonds required in each formula unit. A molecular orbital treatment of this situation could involve sp^3 tetrahedral hybrid orbitals on both the As and S atoms, leading to six As—S σ bonds, ten Tl—S σ bonds (or their ionic equivalents) and doubly occupied non-bonding σ orbitals on the As atoms. The short As—non-bridge S distances clearly indicate some degree of multiple bonding. Now, the development of $d\pi$-$p\pi$ bonding is a marked feature of many compounds and groups formed of combinations of the lighter members of the chemical groups V and VI (COTTON and WILKINSON, 1966), leading to shorter interatomic distances than expected for single bonds, and we can refer these shorter As—S distances to the overlap of the "non-bonding" sp^3 hybrid orbital on the As atoms with the empty d_{z^2} and $d_{x^2-y^2}$ orbitals on the S(1) and S(2) atoms. This would necessitate some modification of the concept of four symmetrical sp^3 tetrahedral hybrid orbitals on each As, so that the two orbitals bonded to the bridge S would have a large p character—resulting in a bond angle approaching 90°—and the orbital bonded to the non-bridge S would have a large s character allowing the fourth to be essentially a p orbital for π-bond formation with the d orbitals on the non-bridge S. It follows that the short As—non-bridge S bonds in other sulfosalts may reflect some degree of multiple-bond formation also.

The nature of the Tl—S bonds represents a more difficult problem. A convenient explanation is to resort to the ionic model with Tl^+ ions coordinated to $As_2S_4^{--}$ ligand groups; the Tl^+ ions being preferentially attracted toward the electron-rich areas of the ligands, i.e. toward the lone pair electrons on the S atoms. The Tl—S distances for the structure range over values similar to those reported for what is assumed to be Tl^+ coordinated with S in Tl_2S and TlS, and the average value for the closer bonds is similar to the expected bond distance for such a model, obtained from the sum of the ionic radius of Tl^+ (1.40 Å) and the van der Waals' radius of S (1.85 Å). The large variation in the nearest Tl—S distances could be ascr.bed either to variation in the disposition of the lone pair orbita's on the S atoms or to the polarizability of the relatively large Tl^+ ions.

However, the Tl—C bonding in the compound TlC_5H_5 has been shown to be largely covalent (SHIBATA, BARTELL and GAVIN, 1964)

and good arguments can be advanced in favor of the Tl—S bonding
in lorandite being largely covalent in character also. The principal
features suggesting covalency are the small difference in the electro-
negativities of Tl (1.8) and S (2.5) and the short Tl—Tl distances,
suggestive of bonding interactions between the Tl atoms. The Tl—Tl
distance in crystalline Tl is 3.457 Å (BARRETT and MASSALSKI, 1966)
so that the short Tl(2)—Tl(2) distance in lorandite represents a bond
number approaching unity. It is clear from the earlier discussion
that Tl—Tl interactions are very common in compounds of Tl with
group VI elements. A closer analogy for the present purpose is tetra-
meric thallium methoxide $(TlOCH_3)_4$ in which the O is coordinated
tetrahedrally to three Tl and one CH_3 group giving intramolecular
Tl—Tl distances of 3.84 Å (DAHL, DAVIS, WAMPLER and WEST, 1962).
In the covalent model, then, recognizing the apparent fivefold coor-
dination of Tl, each Tl would form $sp^3d_{x^2-y^2}$ square-pyramidal
hybrid orbitals to bond with the sp^3 hybrid orbitals on the S atoms.
The two (original $6s^2$) electrons residing on each Tl would be distributed
in different ways, partly occupying antibonding orbitals to the square-
pyramidal σ orbitals, effective to different extents in each internuclear
direction to explain the variation in Tl—S bond lengths, and partly
occupying a low-lying $6d$ or $7s$ orbital for interaction with neigh-
boring Tl atom(s) or for more feeble interactions with more distant
S and As atoms.

Acknowledgement

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